Pigments and inadvertent polychlorinated biphenyls (iPCBs): Advancing no and low iPCB pigments for newsprint, and paper and paperboard packaging

Northwest Green Chemistry

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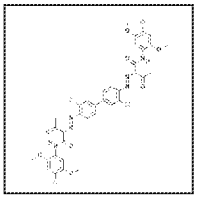
Outline



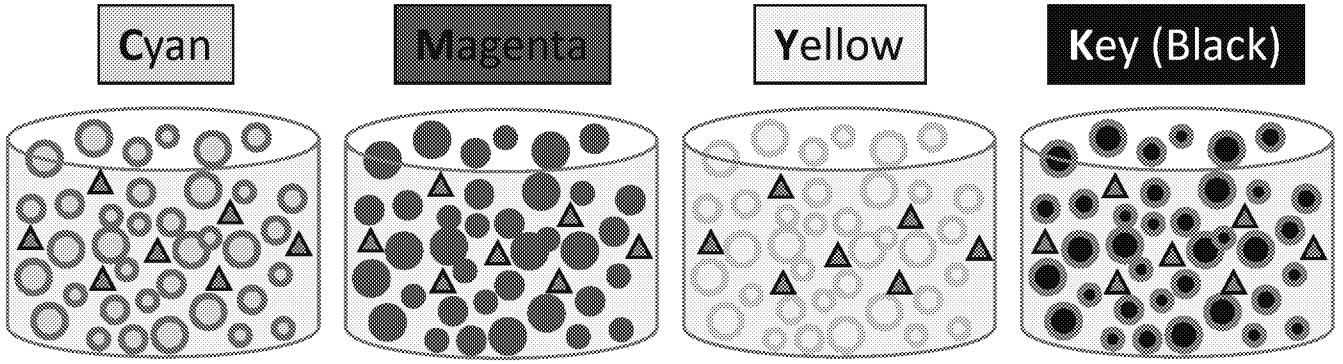
The Chemistry Side

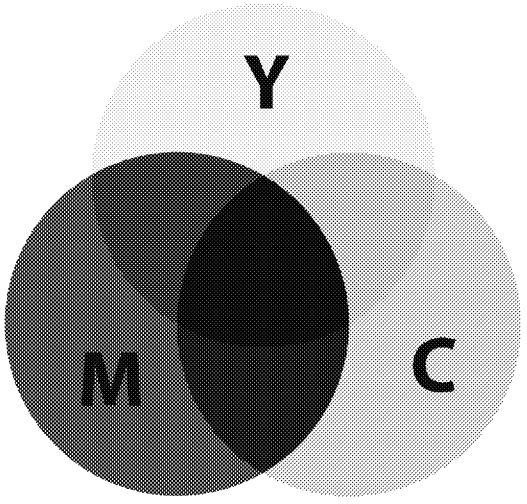
- Performance of pigments for printing inks
- What pigments are currently used?
- How are iPCBs involved in these pigments?
- No or low iPCB options for
  - Yellow pigments
  - Blue/green pigments

Procurement policies and regulations

- Supply chain
- Regulations
- Procurement policies
- Promising practices

Printing ink performance
Example: CMYK color printing





Pigment

embedded in

Resin

dispersed in

Solvent

with performance-enhancing

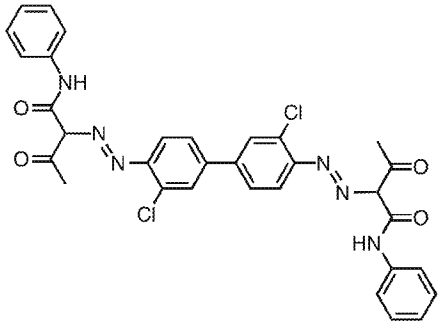
Additives

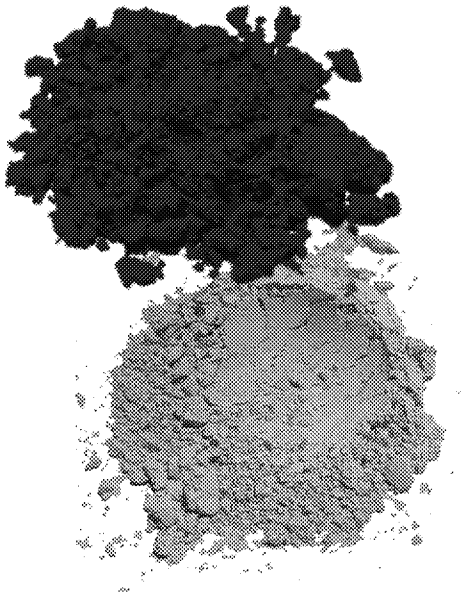
- Transparency / opacity
- Color strength, color power
- Color consistency / matching
- Adherence
- Gloss
- Viscosity / rheology
- Dispersibility
- Drying time
- Soap or solvent resistance
- UV resistance
- Thermal stability
- Cost

What pigments are currently used for printing inks?

Diarylide yellows:

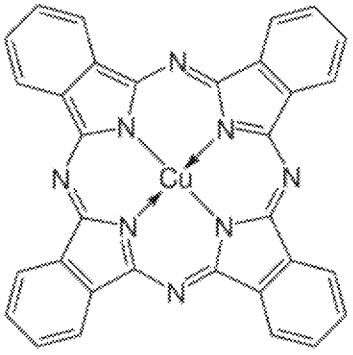
- P.Y. 14 dominates. Green-shade.
- P.Y. 83 – red-shade.
- P.Y. 12, 13, 17 also used.



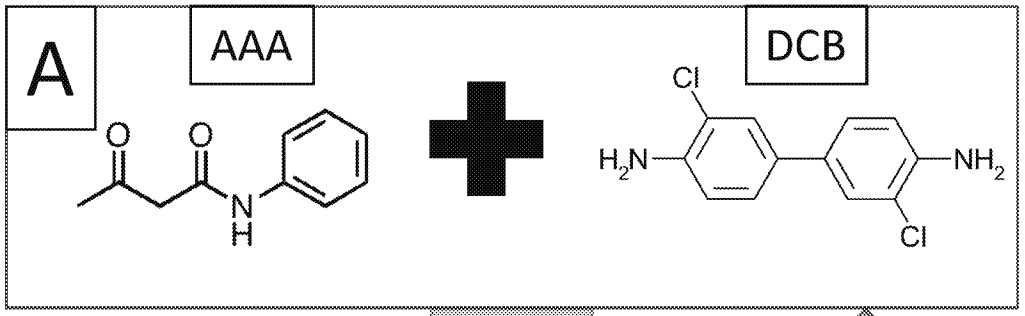


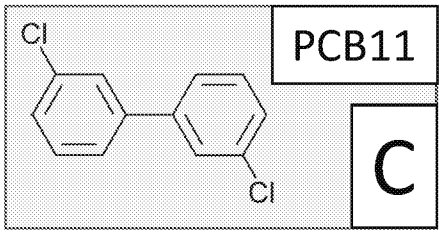
Phthalocyanine blues/greens:

- P.B. 15 dominates. Blue.
- P.B. 15 mixed with yellows often used for green.
- P.G. 7 also used. Green.

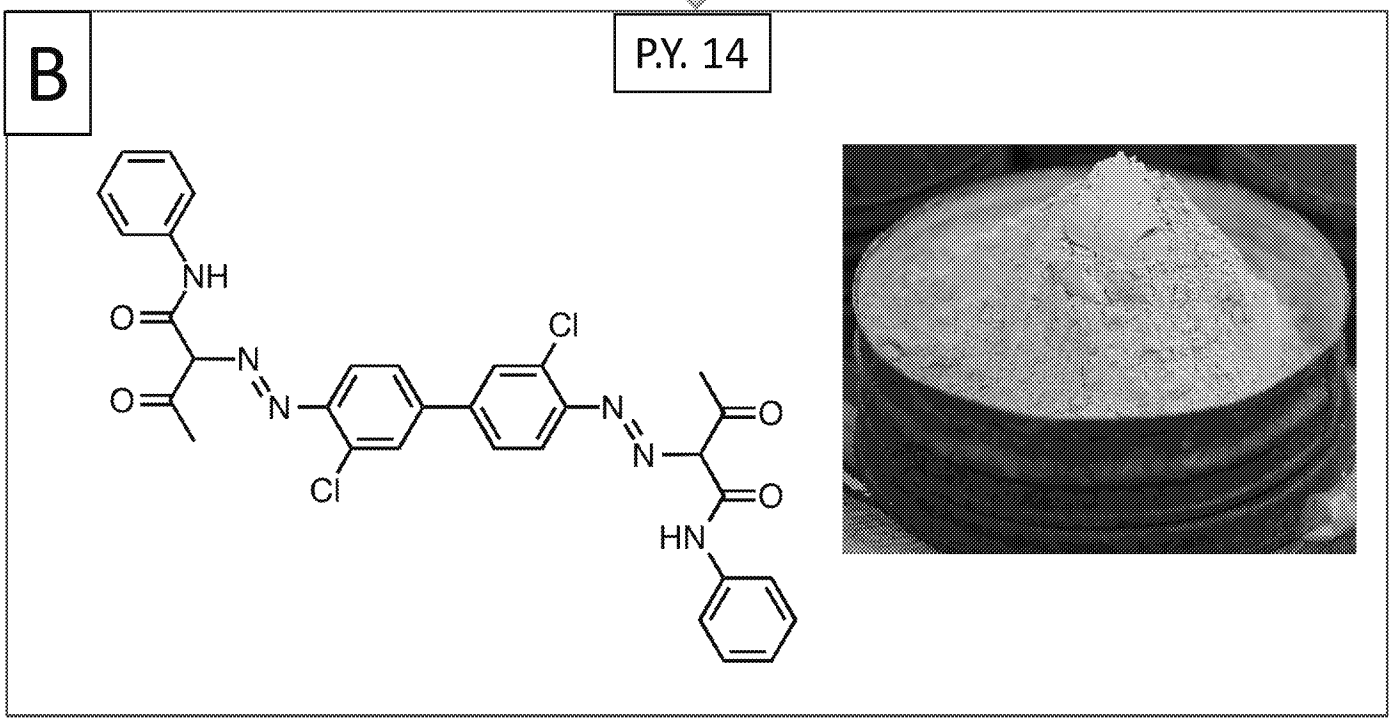


iPCBs: Byproducts from key substrate used for diarylide yellows





P.Y. 14

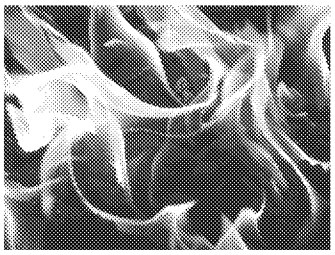


iPCBs: Byproducts from solvent used for phthalocyanine blues/greens

A

Phthalic anhydride

200° C / 400° F



CuCl

Chlorobenzenes

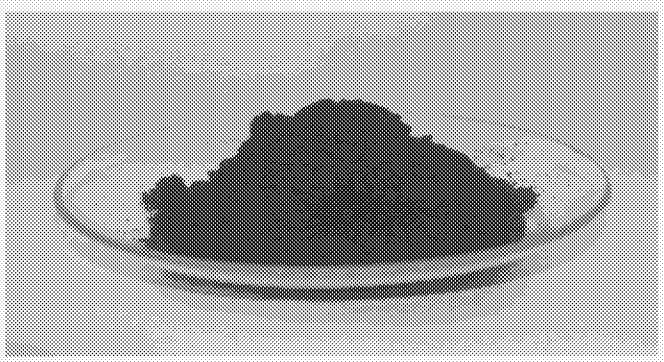
Urea

C

PCB209

B

Pigment Blue 15



Avoiding iPCBs in yellow: Process controls and alternative pigments

3,3'-dichlorobenzidine or other similar compounds are necessary substrates for making ALL diarylide yellows. Can't eliminate.

Process Controls

Pro: No need to reformulate. Same performance.

Con: Cannot eliminate iPCB formation. Not clear the extent to which all manufacturers achieve best practices.

Alternative pigments.

Pro: May essentially eliminate iPCB formation. Alternatives resist UV better.

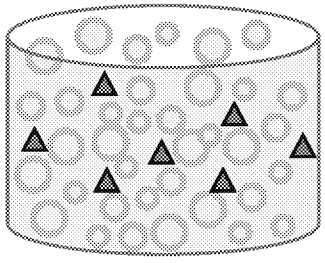
Con: Need to reformulate. Decrease color strength, increase expense. Availability?

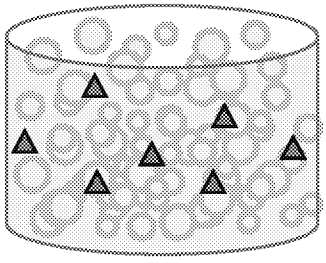
Downsides of switching from diarylides to alternatives

Status quo: diarylide yellows

Monoazo or bisacetoacetarylide alternative pigments

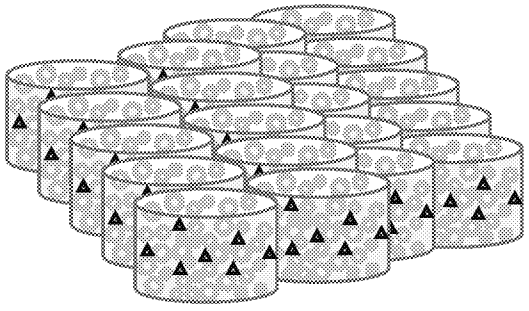
Decreased color strength means more pigment used, which can impact other performance properties

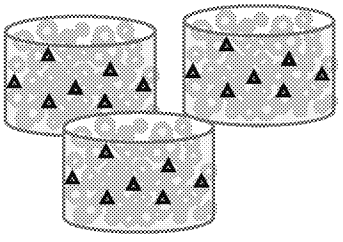




Alternatives are more expensive by cost per pound

Global supply of alternatives is limited. Can we ramp up supply enough for the printing ink industry?



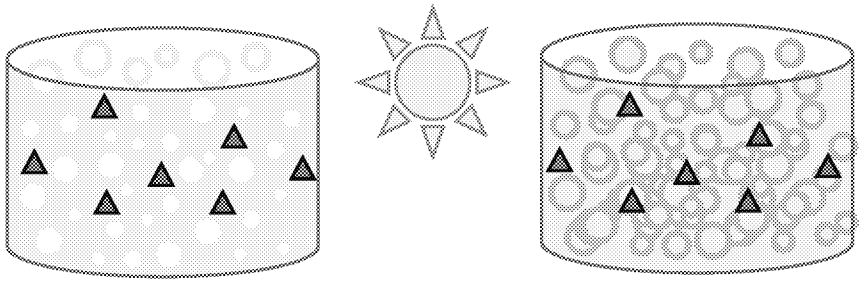


Upsides of switching from diarylides to alternatives

Status quo: diarylide yellows

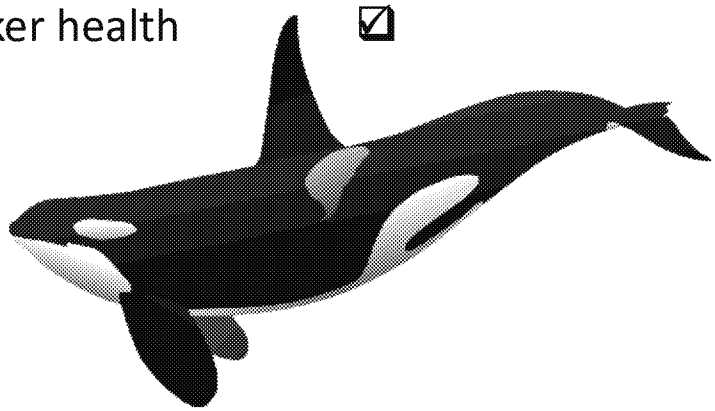
Monoazo or bisacetoacetarylide alternative pigments

Alternatives have improved UV resistance and are currently used as printing inks when this is a priority (e.g. billboards)



Improved environmental (fish, fish predators such as orcas) and human health (high fish consumers, workers)

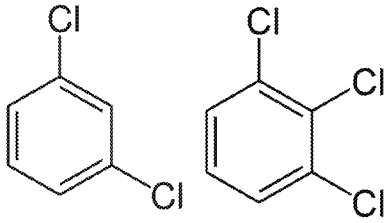
- ❑ Improve circularity ☑
- ❑ Decreased PCBs in fish ☑
- ❑ Decreased PCBs in orcas ☑
- ❑ Improved fish consumer health ☑
- ❑ Improved worker health ☑



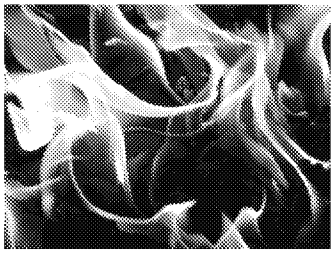
Avoiding iPCBs in the synthesis of blues/greens

- There are no alternative blue/green pigments with the right performance characteristics and cost
  - Cobalt blue: Huge increase in cost. Only used when photobleaching is an issue.
- iPCBs are generated by the presence of chlorine, heat, and the di- or tri-chlorobenzene solvent.

Chlorobenzenes



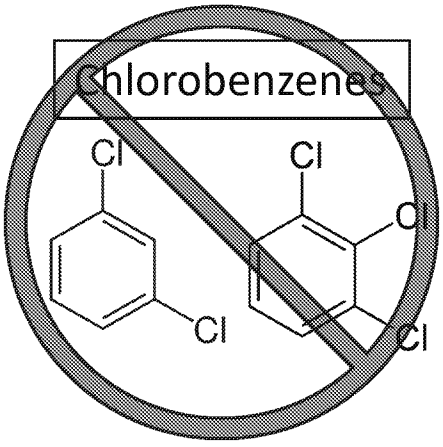
Heat



Chloride ions

CuCl

- iPCB generation can be avoided by:



Kerosene

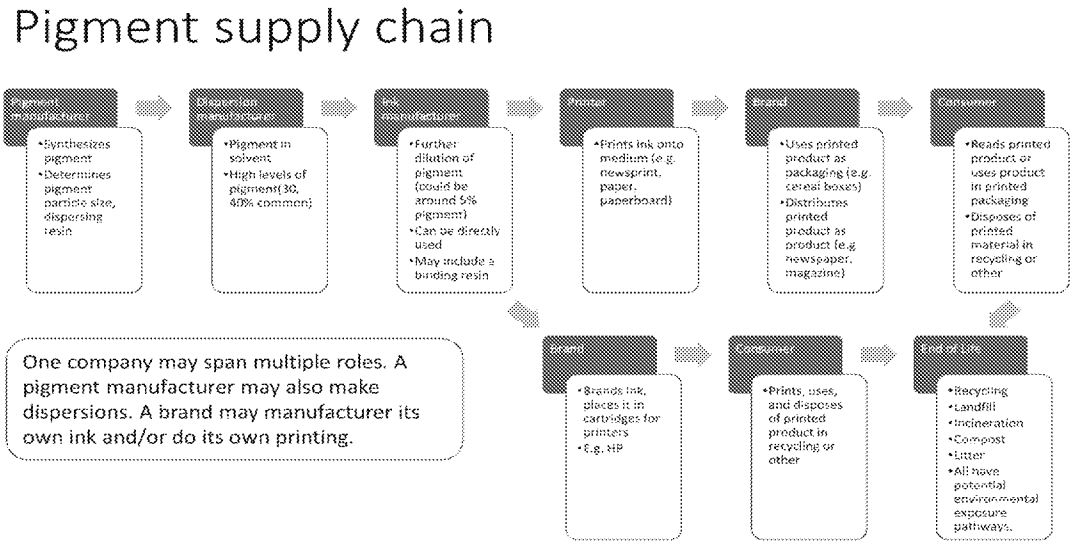
Naphthalene

Other alternative solvents

Dry bake – no solvent

Exploring existing efforts to control iPCB levels: Pigment life cycle

See Figure 8



Exploring existing efforts to control iPCB levels: Regulations *See table 2*

Regulation	TSCA	Stockholm Convention	U.S. Tribal positions	CWA
Applies to	Pigments	All products	Pigments	Water quality
PCB limit	25 ppm average / 50 ppm max; mono- and bi-chlorinated phenyls discounted	As implemented by parties; some have no clear limit while others implemented similar to TSCA	Some tribes propose 0 ppm limit in TSCA	1.37 ppq (Spokane Tribe), 7 ppq (Washington State), 64 ppq (federal)
Address iPCBs in pigments?	Yes	Intended to; main convention documents do not explicitly call out iPCBs in pigments	Yes	Yes, applies to PCBs from any source that enter the designated water body

Exploring existing efforts to control iPCB levels: Procurement

See table 3

Policy	Washington State	City of Spokane	ETAD	HP	Apple
PCB Limit	0 ppm	0 ppm	Meet regulations; encourages best practices	<0.1 ppm	<0.1ppm
Product level	Product purchased	Product purchased	Pigments	All products, verification at pigment level in progress	All products, verification at pigment level in progress
Testing	Required	Optional	N/A	Upon request	Upon request
Products covered	All products likely to contain iPCBs, large purchases only; legislation includes all products	Ordinance does not specify which products; the intent is all products	Pigments	All products	All products
Guidance	Detailed guidance and training for procurement specialists, clear language in request for bids	Very little guidance developed, but request for bids included test method details	Identifies conditions likely to result in iPCB formation	Procurement specifications are detailed overall, but pigments/ iPCBs in progress	Procurement specifications are detailed overall, but pigments/ iPCBs in progress
Current status	Preference only; at least one bid successful (road paint) and one did not receive any testing results (food packaging)	Unenforced currently; first request for bids (deicer) received no bids	Level of compliance by members is unknown	Verification in progress; suppliers have not indicated that compliance will be an issue	Verification in progress; suppliers have not indicated that compliance will be an issue

Promising practices and opportunities

Regulations

PCB limits

Verification

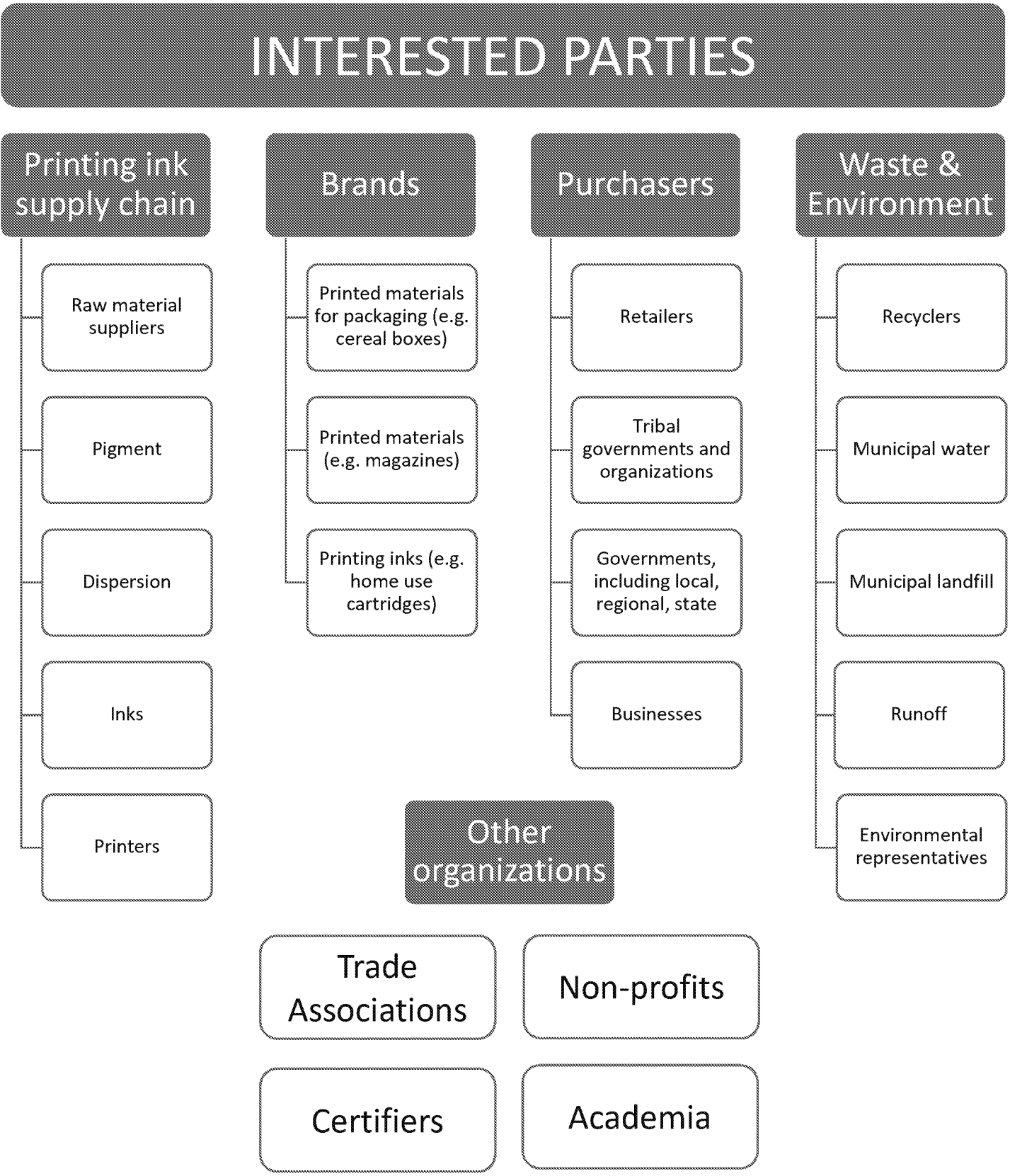
Certification

Supply chain engagement

Availability

Unified procurement policy

Need: Workshop to discuss and take action


INTERESTED PARTIES
Printing ink supply chain
Raw material suppliers
Pigment
Dispersion
Inks
Printers
Brands
Printed materials for packaging (e.g. cereal boxes)
Printed materials (e.g. magazines)
Printing inks (e.g. home use cartridges)
Purchasers
Retailers
Tribal governments and organizations
Governments, including local, regional, state
Businesses
Waste & Environment
Recyclers
Municipal water
Municipal landfill
Runoff
Environmental representatives
Other organizations
Trade Associations
Non-profits
Certifiers
Academia